FINAL REPORT

CATALYST LIFETIME TESTING FOR METHANOL SYNGAS CONDITIONING

Contract Number XAE-3-13442-01

Prepared by
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Final Report for 1995

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Submitted to:

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FINAL REPORT

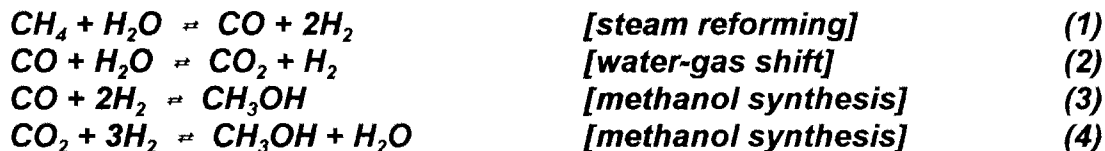|	
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Principal Investigators:	Dr. Sefa Yilmaz and Dr. Scott W. Cowley
Subc. Administrator:	Pat Weitzel
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1.0 BACKGROUND

1.1 Methanol as a Clean Althernative Fuel

Methanol is a clean burning alternative to conventional hydrocarbon based fuels, such as automotive gasoline. It is also considered to be a stategic fuel which can be produced from largely untapped, nonpetroleum resources such as biomass.

1.2 Methanol Synthesis

Methanol is commonly manufactured by first steam reforming of natural gas (primarily CH_4) over a nickel based catalyst to produce a synthesis gas which is subsequently converted to methanol over a copper based catalyst. Details of this process have been reviewed in the literature.*(Ridler, 1989; Saterfield, 1991)* This technology is well extablished The reactions of importance are listed below:

$$CH_4 + H_2O \rightleftharpoons CO + 2H_2 \qquad \textit{[steam reforming]} \qquad \textit{(1)}$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \textit{[water-gas shift]} \qquad \textit{(2)}$$
$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \textit{[methanol synthesis]} \qquad \textit{(3)}$$
$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \textit{[methanol synthesis]} \qquad \textit{(4)}$$

The synthesis gas used to manufacture methanol typically contains CO, CO_2, CH_4, and H_2. The steam reforming process is optimized to minimize or eliminate CH_4 in the product gas and yet produce the appropriate H_2/CO ratio for the manufacture of methanol. The methanol synthesis process requires the following stoiciometry for the partial pressures of the reactants.

$$P_{H2} = 2P_{CO} + 3P_{CO2} \qquad \textit{(5)}$$

Theoretically methanol synthesis requires the partial pressure of H_2 to be equal to twice the partial pressure of CO and three times the partial pressure of carbon dioxide. However, under normal synthsis conditions the hydrogen partial pressure is maintained

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in slight excess of the required stoiciometry.

1.3 Biomass as a Source of Synthesis Gas

Biomass can be pyrolyzed at high temperatures into a synthesis gas which potentially can be used for the manufacture of methanol. Biomass derived synthesis gas contains particulate matter, methane, and pyrolysis tars, in addition to the desired carbon monoxide, carbon dioxide, and hydrogen products. A complete analysis is presented in **table 1.** Commercial nickel based catalysts ($Ni/\alpha-Al_2O_3$) exhibit good activity and durability for the steam reforming of natural gas or naphtha. However, when these catalysts are applied to the steam reforming of a biomass derived pyrolysis gas, they undergo rapid deactivation. The exact cause of the deactivation was unknown.

Table 1. Composition of Biomass Derived Syngas Product

Compound	Mole %
H_2	15.8
CO	23.0
CO_2	9.2
CH_4	9.1
C_2H_2	0.4
C_2H_4	3.0
C_2H_6	0.3
TAR	0.2
H_2O	39.0

2.0 OBJECTIVES OF THIS WORK

The primary objectives of this study are 1) to determine the source of the catalyst deactivation in the presence of biomass derived synthesis gas, and 2) to determine the reaction conditions or catalyst improvements required to eliminate this problem.
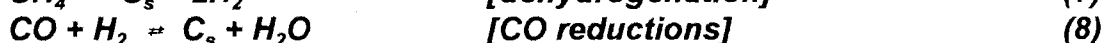
3.0 LITERATURE REVIEW

3.1 Deactivation of Steam Reforming Catalysts by Coking

Current steam reforming catalysts are deactivated by the deposition of solid carbon

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onto the nickel surface, refered to as "coking". Coking can occur via three routes: whiskers or filamentous carbon, encapsulating carbon, and pyrolytic carbon. *(Rostrup-Nielsen, 1984; Rostrup-Nielsen, 1985)* Carbon whiskers are formed at temperatures above 450°C. The biomass derived synthesis gas contains carbon monoxide, carbon dioxide, methane, olefins, and aromatics (tars). All of these carbon based compounds are potential candiates for the source of catalyst coking.

Surface carbon (C_s)can be formed on the exposed nickel surface via CO disproportionation (equation 6), methane dehydrogenation (equation 7), or carbon monoxide reduction (equation 8).

$$2CO \rightleftharpoons C_s + CO_2 \qquad \textit{[disproportionation]} \qquad (6)$$
$$CH_4 \rightleftharpoons C_s + 2H_2 \qquad \textit{[dehydrogenation]} \qquad (7)$$
$$CO + H_2 \rightleftharpoons C_s + H_2O \qquad \textit{[CO reductions]} \qquad (8)$$

The rate of carbon formation from carbon monoxide is known to be 3 to 10 times faster than from methane. Equations (7) and (8) are not thermodyanmically favored at the high hydrogen and steam partial pressures present during steam reforming; therefore, equation (6) is likely the predominant source of surface carbon if carbon monoxide is the coke source. The surface carbon is thought to enter into the nickel crystal matrix to form a nickel-carbon solution. The carbon diffuses through the nickel particle and nucleates and grows at the unexposed side between the nickel metal crystallite and the support surface. The carbon continues to grow between the nickel crystallite and the support surface and forms a carbon whisker. As the wisker grows it lifts the nickel particle away from the surface of the support and the nickel particle remains on the growing tip of the whisker. Whiskers can grow rapidly inside the void spaces of a catalyst particle and exert sufficient pressure to break apart the catalyst into smaller particles. Eventually the particles become too small and produce an unacceptable pressure drop across the catalyst bed or plug the reactor; thus forcing a shutdown of the system.

Encapsulating carbon, a polymerization product of CH_{2-x} species on the Ni surface, deactivates the surface directly, and the reactions are shown in equations (9) and (10) below.

$$CH_2{=}CH_2 \rightleftharpoons 2(CH_2)_s \qquad \textit{[surface adsorption]} \qquad (9)$$
$$n(CH_2)_s \rightleftharpoons [(CH_{2-x})_n]_s \qquad \textit{[polymerization]} \qquad (10)$$

The letter "**s**" denotes a surface species. Encapsulating carbon forms at temperatures less than 500°C. Pyrolitic carbon is formed above 600°C and is the result of polmerization of olefins and aromatics produced by the thermal or catalytic cracking of hydrocarbons. Biomass derived syngas typically contains ~ 3 to 5 mole percent of ethylene. Support acidity is also known to facilitate cracking reactions which produce olefinic compounds.*(Rostrup-Nielsen, 1984)* All the commercial catalysts develped thus far are subject to carbon deposition under steam reforming conditions. In practice,

carbon deposition can only be prevented by using excess steam, ie. a steam to hydrocarbon ratio in excess of 1.7. Excess steam also promotes the steam reforming reaction, thus steam to hydrocarbon ratios 3.0 to 3.5 are commonly used. Carbon is removed by the reaction of surface carbon with steam or hydrogen, as indicated in equations (11) and (12) below.

$$C_s + H_2O \rightleftharpoons CO + H_2 \qquad \text{[carbon oxidation]} \qquad (11)$$
$$C_s + 2H_2 \rightleftharpoons CH_4 \qquad \text{[carbon reduction]} \qquad (12)$$

The rate of carbon formation depends on the type of hydrocarbon, the catalyst, and the process conditions. Carbon formation strongly depends on the unsaturated character of hydrocarbons. Bridger and Chinchen ranked the relative rates of carbon for a variety of hydrocarbon spieces. *(Bridger and Chinchen, 1970)*

> ethylene >> benzene, toluene > n-heptane > cyclohexane >
> trimethyl butane ≈ n-butane ≈ carbon monoxide > methane

Although a lot of information is available in the literature about steam reforming of saturated hydrocarbons, relatively little information is found with respect to steam reforming of aromatic or unsaturated hydrocarbons. Biomass pyrolysis gas contains both aromatic and unsaturated hydrocarbons. There is a strong possibility that the aromatic and olefinic compounds present in biomass pyrolysis gas are responsible for the deactivation observed when using biomass derived feedstocks.

3.2 Poisoning of Ni Metal by Trace Contaminants in Synthesis Gas

Several trace contaminants present in biomass pyrolysis gas are known to deactivate supported metal catalysts, and include sulfur, arsenic, lead, and chlorine. For example, a biomass derived syngas obtained from wood is reported to contain < 100 ppm of chlorine, < 0.1 ppm of arsenic, and 1.0 ppm of lead. Catalyst deactivation caused by arsenic and lead contaminants in the synthesis gas could be substantially reduced or eliminated by placing an inexpensive guard bed or a high temperature filter (assuming they are present in the form of particulates) in front of the nickel based steam reforming catalyst bed.

Recent work by Ortego, Richardson, and Twigg has shown that chlorinated compounds can be steam reformed using conventional nickel based catalysts. *(Ortego, Richardson, and Twigg, 1996)* They found that chlorine inhibited the steam reforming reaction, but the effect was reversible. Base on their work, one can conclude that the small amount of chlorine present in biomass derived synthesis gas should not be the source of catalyst deactivation.

Deactivation by sulfur poisoning is the other important deactivation process for steam reforming catalysts. Industrially, sulfur in the form of H_2S is removed in a desulfurization unit by converting ZnO into ZnS. Organic sulfur compounds (mercaptans and thiophenes) are hydrotreated over a Co-MoS_2 based catalyst to

produce H_2S which is subsequently removed in the ZnO desulfurization unit. Sulfur poisoning is well documented in the literature.*(Rostrup-Nielsen, et al., 1992; Numaguchi, and Kikuchi, 1991; Marecot, et al., 1992; Aguinaga, et al., 1992; Demicheli, et al., 1994)* Nickel metal is known to combine with hydrogen sulfide to form a catalytically inactive nickel sulfide. However, the nickel surface can be completely poisoned by forming a sulfur monolayer at ppm leverls much lower than is required to form the bulk metal sulfide. This poisoning process is reversible but strongly favors the adsorbed sulfur compound at equilibrium, see equation (13) below.

$$Ni + H_2S \rightleftharpoons NiS_{(monolayer)} + H_2 \qquad \textit{[surface poisoning]} \qquad (13)$$

The equilibrium position is improved by higher hydrogen partial pressures and higher reaction temperatures. It is worsened by higher hydrogen sulfide partial pressures. Biomass derived pyrolysis gas contains about 1 ppm of sulfur. This amount is unlikely to cause severe deactivation. In fact, a small amount of sulfur is helpful in retarding the carbon deposition reactions.

4.0 EXPERIMENTAL PROCEDURE

4.1 Synthetic Pyrolysis Gas Feedstock
The objective was to introduce a synthetic gas mixture that simulated the pyrolysis gas mixture generated by the biomass gassifier at Battelle Institute in Richland, Washington. Two synthetic pyrolysis gas mixtures were purchased from Matheson Gas Products. The first mixture contained 25.99 % H_2, 38.00 % CO, 15.00 % CH_4, 15.00 % CO_2, and 6.01 % Ar on a mole % basis. It is important to note that this synthetic mixture has no olefinic component. Argon was used as an internal standard. The second mixture contained 25.86% H_2, 38.33% CO, 14.97% CH_4, 14.89% CO_2, 4.96% C_2H_4, 0.50% C_2H_2, and 0.49% C_2H_6 on a mole % basis. In this case the argon was replaced with the C_2 compounds ethylene, acetylene and ethane.

Water vapor was introduced by bubbling one of the two gas mixtures through two stainless steel saturators in series. The saturators are housed in a temperature controlled oven to provide the desired saturation temperature. An oven temperature of 68°C for the saturators and a gas hourly space velocity of 5000 cc gas/cc catalyst-hr gave a final gas mixture containing 30 mole % water. The use of two synthetic gases allowed the study of a synthetic feedstock with and without an olefinic component.

A second saturator maintained at 0°C was used to introduce toluene into the water-saturated mixture. Helium gas was bubbled through the saturator containing toluene at a flow rate sufficient to produce a 2.5 mole % concentration of toluene in the final mixture. The composition of the gas feedstock was verified by GC analysis.

4.2 Gas Chromatographic Methods Employed
The composition of the product gas was determined by two on-line gas chromatographs

that were placed in series. The first GC contained a Carboxeen 1000 column and a thermal conductivity detector for analysis of the gaseous products H_2, CH_4, CO, CO_2, C_2H_2, C_2H_4, C_2H_6, and H_2O. The second GC contained a column containing 10 weight % SP 2100 on Supelcoport and an flame ionization detector for analysis of the higher molecular weight aromatic compounds.

4.3 Steam Reforming Apparatus

The steam reforming apparatus that was used in the previous year was modified in order to introduce the liquid components without pulsing, see *figures 1 and 2.* The apparatus is an up-flow tubular reactor with two electrical ovens. The first oven is for preheating the reaction mixture to 300°C and the second oven is for the steam reforming reaction and is operated between 700 and 815°C. The reaction mixture was introduced at the bottom of a quartz tube that contained a porous fritted disk which was located at the bottom of the isothermal region of the second oven. Approximately 200 mg of catalyst was placed on top of the fritted disk. The gas mixture was passed through a two saturators in series containing water. A saturator temperature was selected to give the desired mole % of water in the reaction mixture. A second saturator was used to blend a helium-toluene gas mixture with the water saturated gas mixture. The reaction products were analyzed by two on-line gas chromatographs. The test sequence was programmed into a computor and all reaction variables were controlled and monitored by a computor.

4.4 Experimental Procedure for Catalyst Deactivation

An experimental testing sequence was developed to test deactivation of UCI G90B at different feed compositions. A 200 mg sample of the catalyst was mixed with 1.8 g of DN-50 diluent and exposed to a simulated syngas feedstock at 5050 VHSV (volume hourly space velocity) for all the tests. To determine which compounds have the highest propensity to deactivate the catalyst, all tests are carried out at identical reaction conditions, only the composition of the feed was varied. In one experiment, for example, a feedstock containing hydrogen, carbon monoxide, carbon dioxide, methane, ethyne, ethene, ethane and toluene was steam reformed. In a separate experiment a mixture containing hydrogen, carbon monoxide, carbon dioxide, methane and toluene was steam reformed under identical reaction conditions. In the latter mixture the C_2 compounds were removed in order to observe the effect of unsaturated compounds (ethene and ethyne) on the rate of catalyst deactivation. Ethane was also removed because it can be a precursor to ethene. Argon was added to the feedstock to replace the components removed to keep the composition of the other components constant. This test allowed us to compare reaction product compositions in the absence and the presence of olefinic and acetylenic components. The following test sequence was used:

a)   The feedstock flow rate was allowed to reach steady state at 250 °C, a temperature at which the steam reforming reaction is insignificant.

b)   The steam reforming reaction was conducted at 800 °C for 15 hours.

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c)   The steam reforming reaction was conducted at 750 °C for 17 hours to accelerate the coking pr°Cess.

d)   The reaction temperature was returned to 800 °C for 8 hours to measure the degree of deactivation that °Ccured at 750 °C and to check for signs of catalyst regeneration.

e)   The reaction temperature was reduced to 750 °C for 3.5 hours to measure the degree of deactivation that °Ccurs during the 800 °C test condition.

f)   The reactor temperature was decreased to 250 °C to make sure that inlet compositions and flow rate did not change during the test sequence.

After each experiment, tested catalyst was analyzed by XRD and light microscopy.

5.0 EXPERIMENTAL RESULTS

5.1 Permanent Gas + Aromatics + Olefins Feedst°Ck

A feedst°Ck composed of H_2 + CO + CO_2 + CH_4 + C_2H_2 + C_2H_4 + C_2H_6 + C_7H_8 (toluene) was steam reformed in the presence of UCI G90B catalyst and a DN-50 diluent. **Figure 3** shows the change in the product composition versus time on stream for this feedst°Ck. The catalyst began deactivating after an exposure of 450 minutes at 800 °C. As shown in **figure 3**, concentrations of H_2 and CO started to decrease and those of CH_4 and CO_2 started to increase at about 450 min. The decrease in H_2 and CO and increase in CH_4 concentrations indicated the start of deactivation. The primary deactivation source under these conditions is coking. During this first 800 °C period for 15 hr, C_7H_8, C_2H_4, and C_2H_6 conversions were 100 % and no benzene was detected, see **figure 4**.

At 750 °C the catalyst deactivated at a faster rate than that at 800 °C. After dropping the reaction temperature to 750 °C, H_2 production started decreasing at a rate approximately four times faster than that at 800 °C. Ethylene and ethane concentrations in the exit stream also started to increase. Methane concentration increased about two times faster at 750 °C than that at 800 °C, but the concentration of CO decreased at about the same rate as that observed at 800 °C. Methane concentration in the exit stream reached 44% of its inlet concentration after 31 hours from the start. This indicates that almost half of the active sites responsible for steam reforming of CH_4 were deactivated. Concurrent with this observation, water consumption also decreased. At 750 °C, C_7H_8 and C_6H_6 (benzene) were also detected in the exit stream and toluene conversion decreased to about 95 mol %, see **figure 4**. Benzene formation suggests that cleavage of methyl group from C_6H_5 ring is one of the steps in the steam reforming of toluene on the Ni catalyst.

When the reaction temperature was returned to 800 °C, the initial activity of the catalyst was not restored since concentrations of H_2 and CO were lower and those of CO_2 and CH_4 were higher than those initially observed at 800 °C, as shown in *figure 3*. Ethylene and ethane conversions were 91 and 72 mol %, respectively. Furthermore, once coke deposited on the catalyst surface, it remained on the surface and initial activity of the catalyst was never recovered under the reaction conditions.

Concentration of H_2 continued to decrease in the second 800 °C period but at a slower rate than that at the previous periods either at 750 °C or 800 °C. Similar behavior was also observed for CH_4 in that its concentration increased at a slower rate than previous periods. Carbon monoxide concentration did not decrease with time in the second 800 °C period. These observations showed that after the catalyst was coked, it still had a residual activity and coking rate of the catalyst was slower than that previously observed. This observation may indicate that the most active sites cokes first and consequently yielding a faster deactivation rate. Finally, less active sites deactivate yielding smaller slopes for H_2 decrease (moles/minute) and CH_4 increase.

As shown in *figure 4*, toluene was not totally converted in the second 800 °C period due to coke deposition on the catalyst. The toluene concentration increased with time but at a rate five times slower than that at the previous 750 °C period. Benzene concentration also increased with time, but the rate of increase was not affected as the temperature was increased from 750 to 800 °C. The benzene concentration appeared to be insensitive to toluene concentration in the gas phase indicating that benzene formation shows a zero order type reaction with respect to gas phase concentration of toluene.

The temperature was dropped to 750°C for the second time to see if any of the catalyst activity had recovered during the second 800°C. Concentration of H_2 decreased at a slower rate than that at the previous 750°C period. Concentration of CO also decreased, but its deceleration rate was the same as that during the previous 750°C period. Toluene concentration increased a rate similar to that during the previous 750°C period, but, interestingly, the benzene concentration first dropped as the temperature decreased, and then it started to increase at a rate twice of that observed during the first 750°C period. The reaction temperature was finally decreased to 250°C to make sure that the feedstock composition did not change duration of the experiment.

In summary, the rate of deactivation was most severe using this gas mixture. The catalyst appeared severely coked. There was evidence that catalyst particles were fracturing as the coking process proceeded. The volume of the catalyst bed nearly doubled in volume due the amount of carbon deposited.

5.2 Permanent Gas + Aromatics Feedstock
The tests with this feedstock showed that olefins are the major source for the deactivation of the catalyst. Deactivation was much less severe after C_2H_2, C_2H_4, and

C_2H_6 were removed from the feedstock. Concentration of H_2, CO, CO_2, and H_2O did not change during exposure to 800°C, but the concentration of CH_4 did increased slightly, see *figure 5*. After the catalyst temperature decreased to 750°C, the H_2 concentration decreased with time, but its rate of decrease was an order magnitude slower than that during the same period in the presence of C_2H_2, C_2H_4, and C_2H_6. The CH_4 concentration continued to increase with a rate three times slower than that during the presence of above olefinic compounds. Upon increasing temperature back to 800°C, the H_2 concentration went back to a slightly lower level than that during the previous 800°C period. This indicated that the catalyst was coked to some degree, but the level of deactivation was not as bad as when C_2H_2, C_2H_4, and C_2H_6 are present. Dropping the reaction temperature back to 750°C did not cause the H_2 concentration to dropped to that during the previous 750°C period.

Toluene conversion was 100% during four temperature periods and no benzene was detected, contrary to that observed with the feedstock containing C_2H_2, C_2H_4, and C_2H_6 (*figure 6*). Apparently, benzene formation is directly related to coking of the catalyst. This may indicate that the toluene destruction reaction may be structure sensitive. The structure sensitivity, where the arrangement of atoms relative to one another is critical, is common where a C-C bond is broken.

5.3 Permanent Gas
Permanent gas feedstock includes H_2, Ar, CO, CH_4, CO_2, and H_2O. As shown in *figure 7*, H_2 and CH_4 concentrations were nearly constant during the reaction period indicating that no deactivation of the catalyst was detectable in the time period of the test.

5.4 Coking of the Catalyst
In all tests carried out with three feedstocks, the tested catalyst was carefully inspected visually and with a light microscope. The tested catalyst and DN50 diluent used with permanent gas + aromatics + olefins feedstock appeared to be totally covered by coke as seen by a naked eye. Light microscope pictures also show that all catalysts particles were covered by coke (*figure 8*). The original bed volume, in the case of permanent gas + aromatics + olefins feedstock, expanded by approximately 77 % due to the coking of the catalyst and the diluent. The catalyst tested with the feedstock containing permanent gas + aromatics was also heavily coked but the diluent DN50 was partially coked (*figure 9*). In this case, the catalyst bed volume expanded by 38%. No coloring of the diluent and no expansion of the bed volume were observed in the catalyst exposed to permanent gases only. However, the tested catalyst had a slightly darker color (*figure 10*).

6.0 ACCOMPLISHMENTS

6.1 Construction of Automated Steam Reforming Reactor
An automated steam reforming reactor capable of operating at temperatures up to 900°C and introducing a feedstock that is uniform in composition, flow and pressure

was constructed and tested. The reactor is capable of operating in the automated mode for several days without supervision. Some of the long term activity studies required two to three days of operation.

6.2 Simulation of a Biomass Pyrolysis Gas

A biomass pyrolysis gas was simulated by mixing H_2, CH_4, CO, CO_2, C_2H_2 (acetylene), C_2H_4 (ethylene), C_2H_6 (ethane), H_2O, and C_7H_8 (toluene). Special saturators were constructed to eliminate the problems of pulsing observed with liquid pumps.

6.3 Testing of DN-34, DN-50, γ-Alumina, and UCI G90B Steam Reforming Catalysts

Biomass pyrolysis gas contains significant amounts of methane, ethylene,and aromatic compounds. It is desirable that these compounds be eliminated via a catalytic steam reforming process prior to contact with a methanol synthesis catalysts. DN-34 is a proprietary catalyst and was obtained from Battelle Research Institute in Richland Washington. It was reported by Battelle to have some activity for the steam reforming of aromatic tar components present in biomass pyrolysis gas. Work conducted at CSM and at NREL found that DN-34 has no steam reforming activity for methane, ethane or toluene, but it does exhibit water-gas shift activity and possibly some steam reforming activity for ethylene. The steam reforming activity of toluene observed at 815°C is due to thermal reactions and occurs in the presence or absence of DN-34. DN-34 was not found to be stable at the reaction temperatures employed in this study and underwent a gradual phase change. XRD analysis showed that DN-34 was gradually converted into γ-alumina. The catalytic activity of the γ-alumina and DN-50 catalysts was found to be identical to that observed for DN-34.

DN-50 contains an α-alumina phase and has the same product selectivity as DN-34 and γ-alumina but it has a much lower activity. The lower activity is because DN-50 has a much lower surface area surface area than DN-34 or γ-alumina.

The UCI G90B steam reforming catalyst shows excellent steam reforming activity, but is quickly deactivated by the presence of unsaturated compounds in the feedstock. Olefins were found to foul the catalyst much faster than aromatics.

7.0 References

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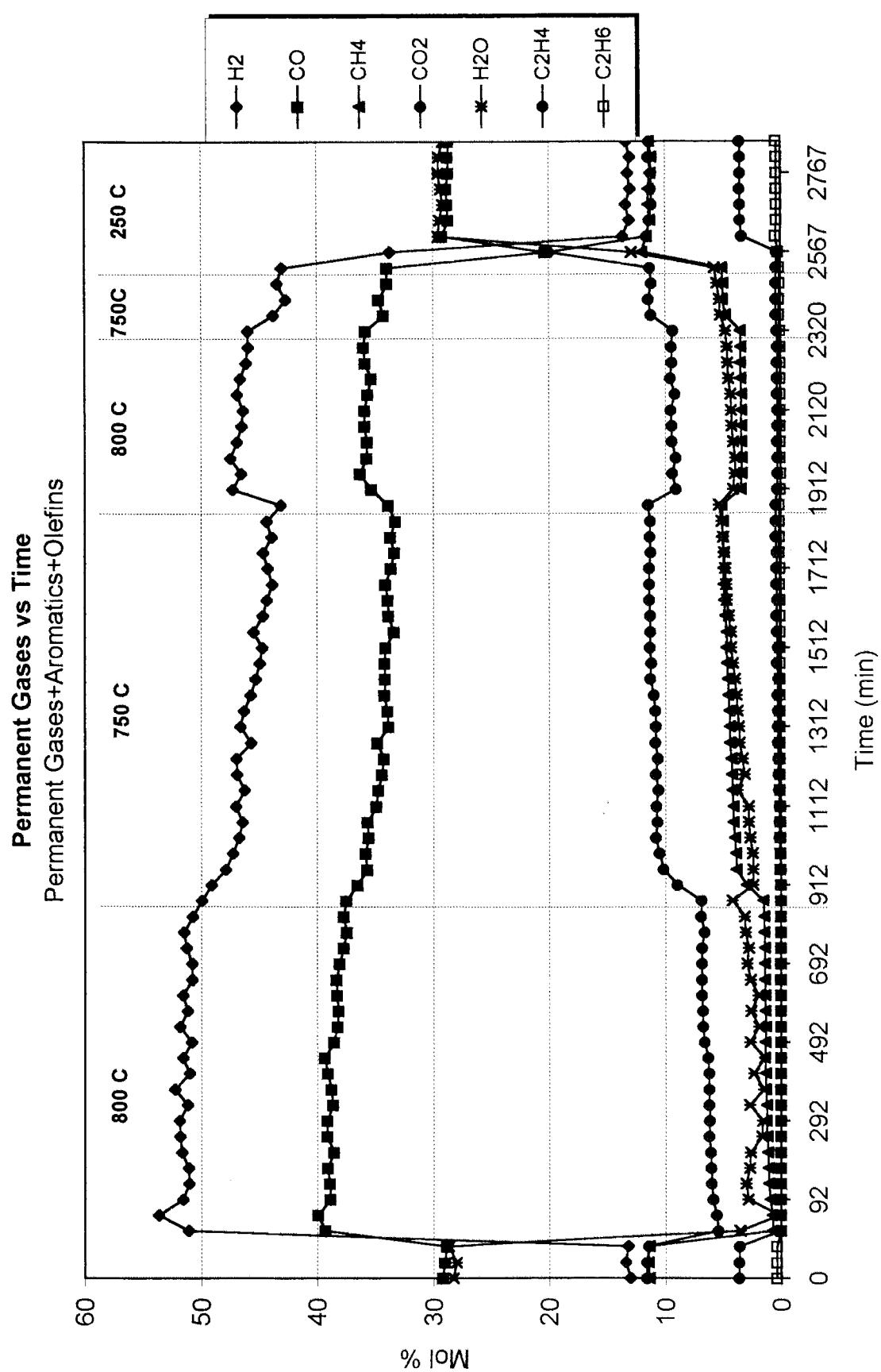
Figure 1. Concentration versus time plot for permanent gases + aromatics + olefins feedstock.
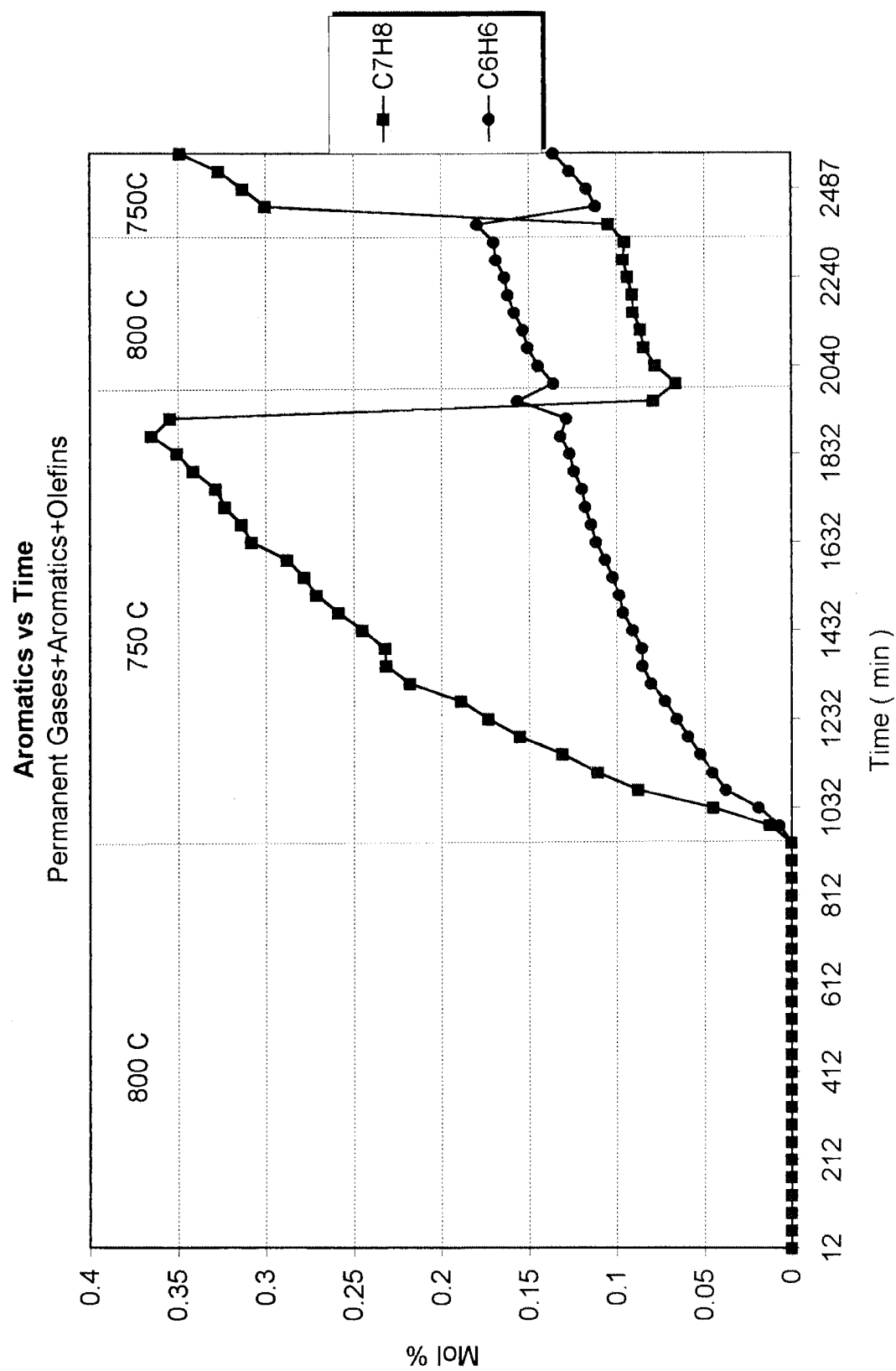
Figure 2. Concentration change of toluene and benzene during exposure of permanent gases + aromatics + olefins feedstock.
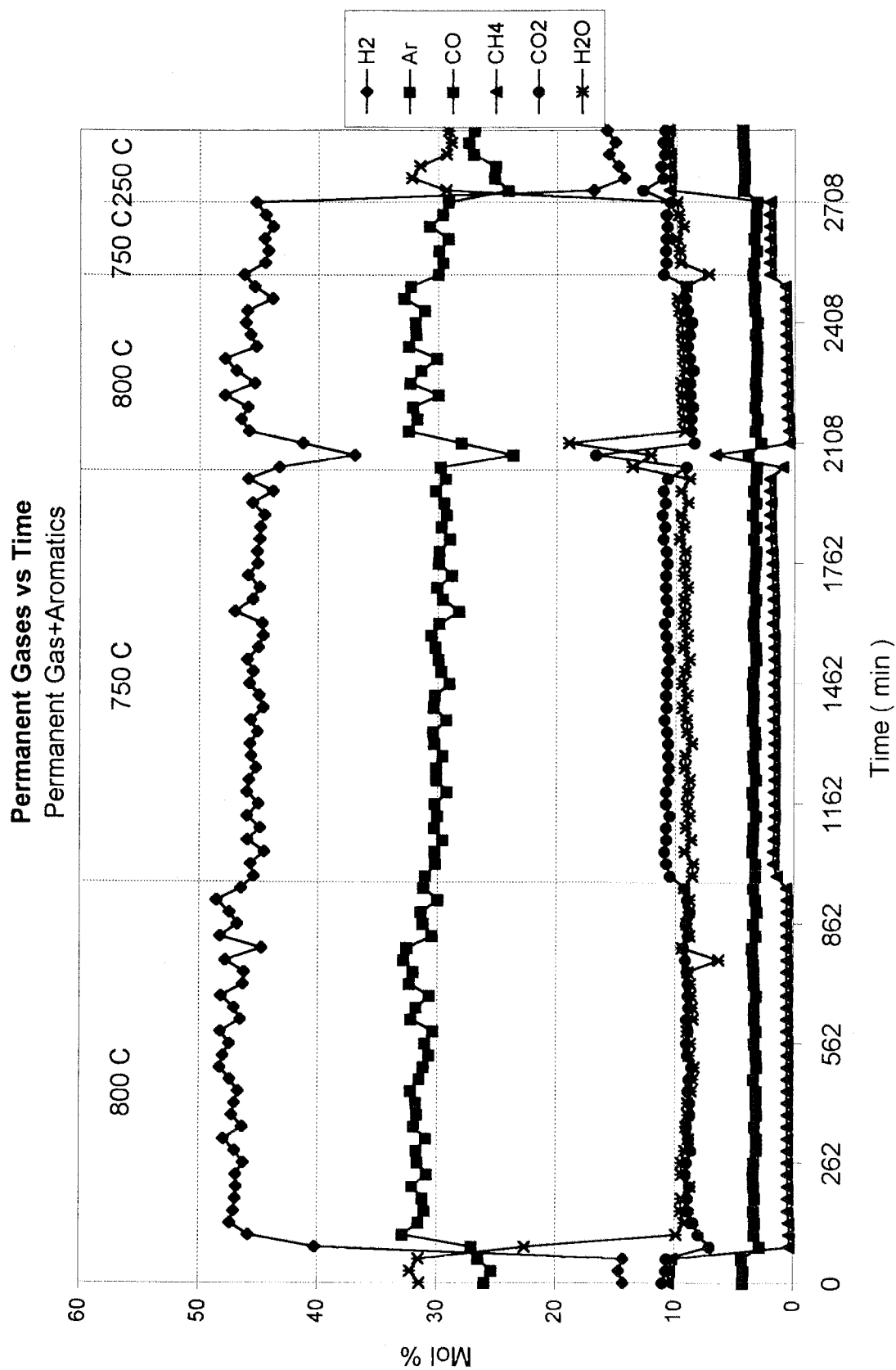
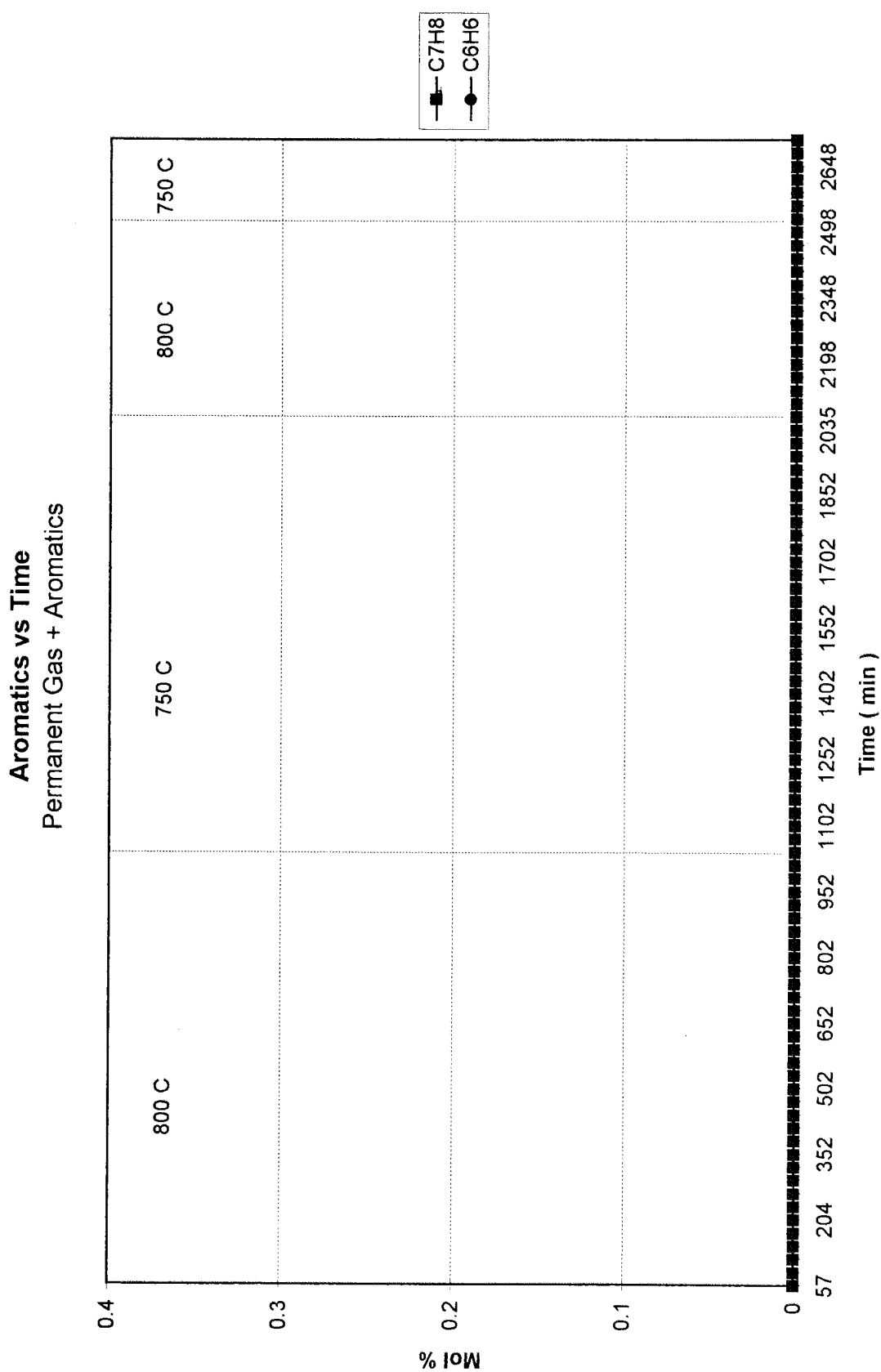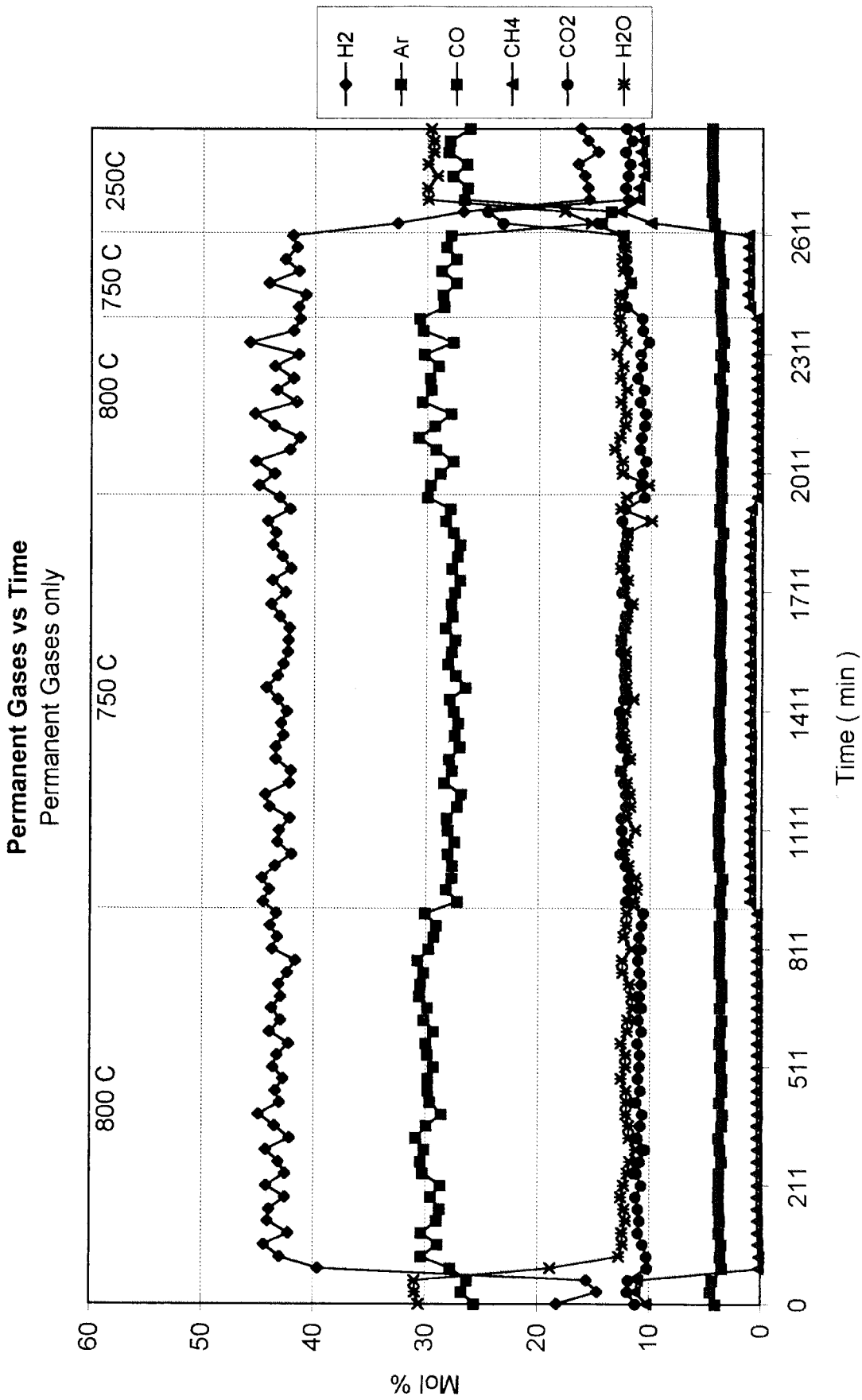Figure 3. Concentration versus time plot for permanent gases + aromatics feedstock.

Aromatics vs Time
Permanent Gas + Aromatics

Mol %

Time (min)

C7H8
C6H6

800 C

750 C

800 C

750 C

Figure 4.   Concentration change of toluene and benzene during exposure of permanent gases + aromatics feedstock.

Figure 5. Concentration versus time plot for permanent gases feedstock.
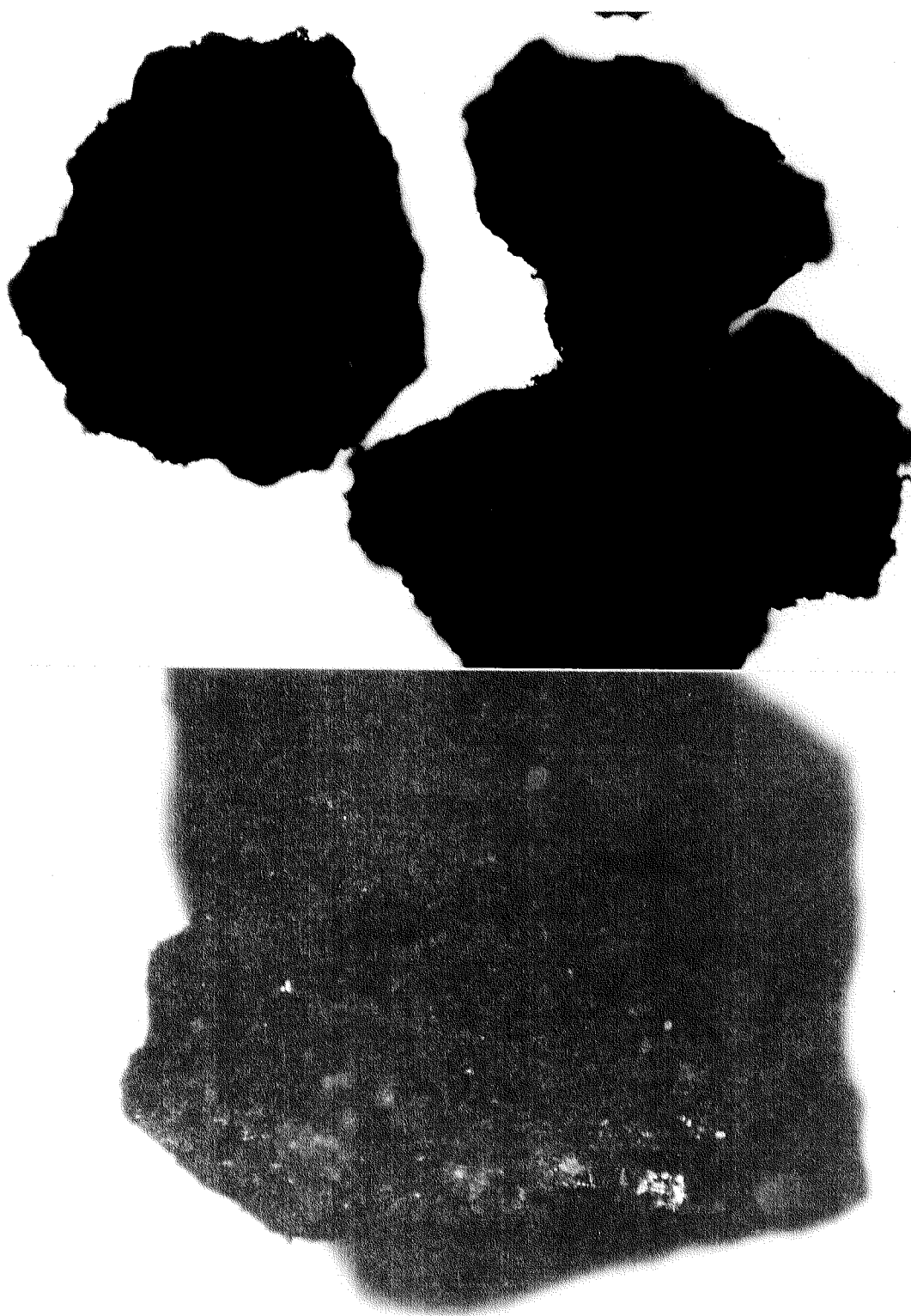
Figure 6. Coked a) catalyst particles, b) DN50 diluent particle after exposure to permanent gas + aromatics + olefins feedstock.
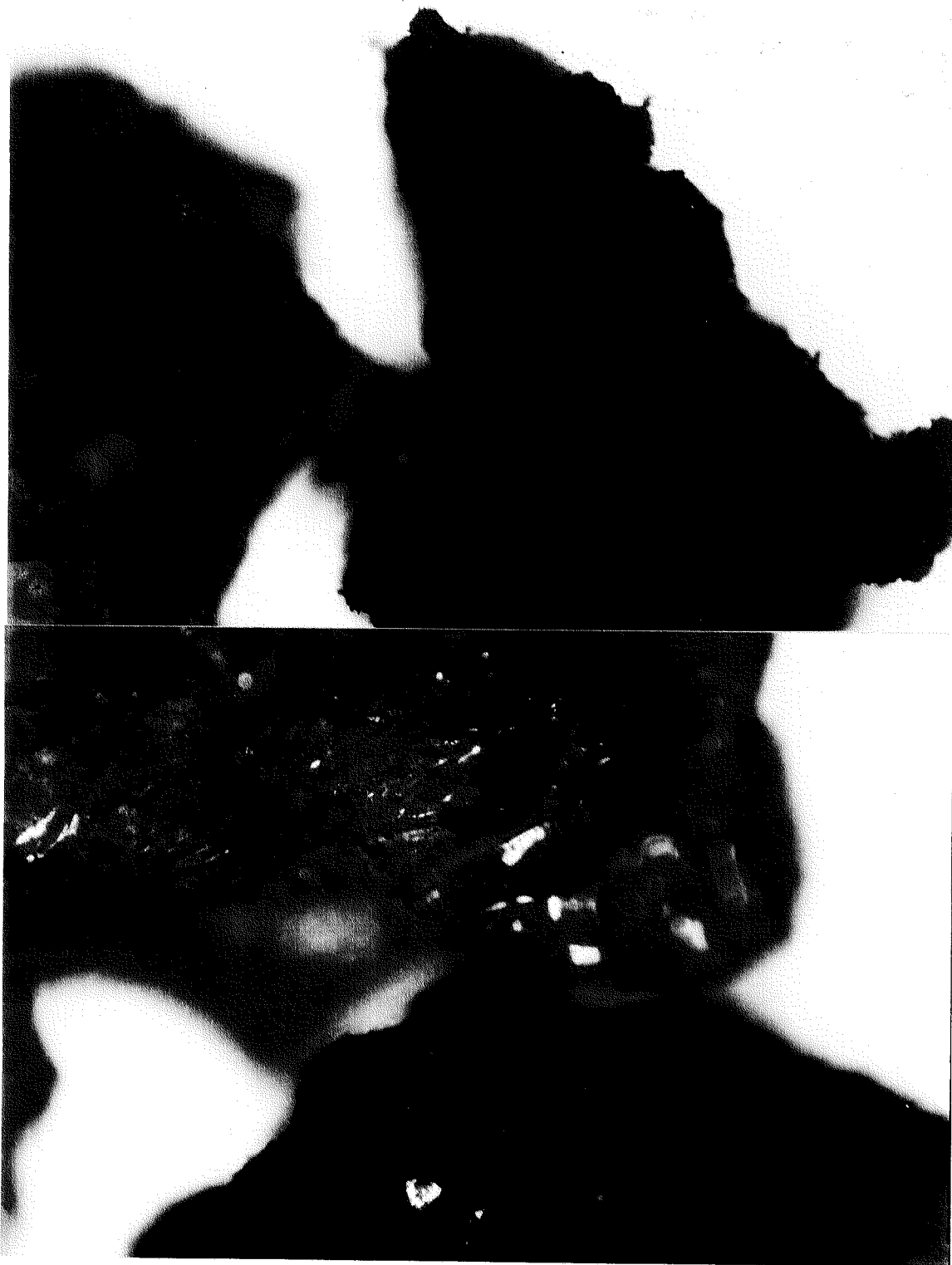
Figure 7. Coked a) catalyst particles, b) DN50 diluent particle after exposure to permanent gas + aromatics feedstock.
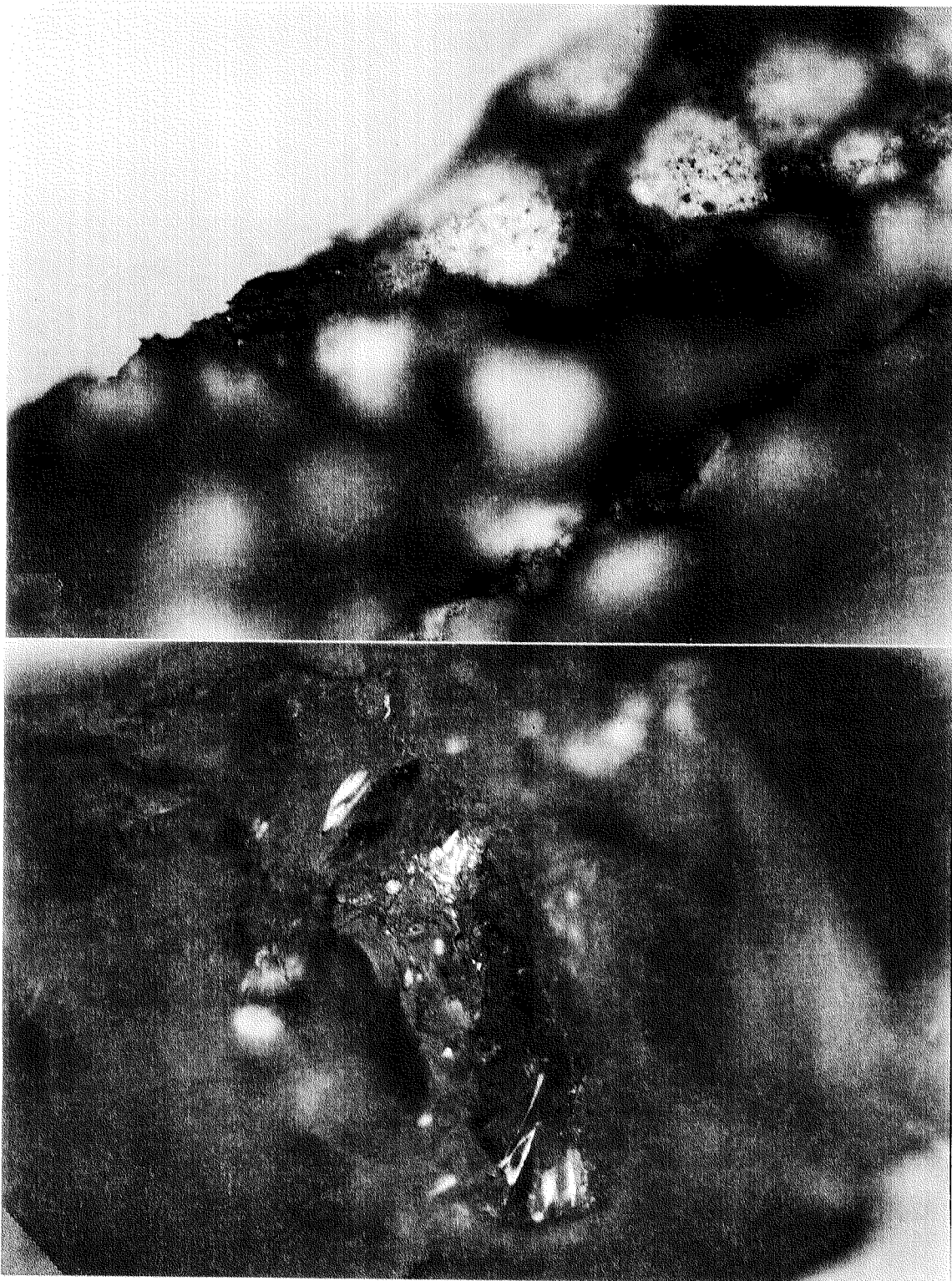
Figure 8. Coked a) catalyst particles, b) DN50 diluent particle after exposure to permanent gas
          feedstock.